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Insight into structure–reactivity relationships for the iron-catalyzed hydrotreatment of technical lignins

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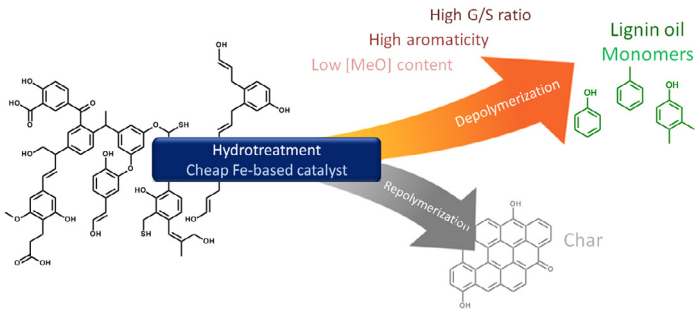
GRAPHICAL ABSTRACT



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ABSTRACT

The viability of several technical lignins as a source for biobased platform chemicals was investigated via hydrotreatment using a cheap Fe-based limonite catalyst and without using a solvent. In general, high-quality oils (up to 29 wt% total monomers) with an average relative composition of 55% alkylphenolics and 27% aromatics were obtained. Detailed structural investigations showed that the S-G aromatic unit content of the lignins was the most important factor positively affecting overall oil yields. A second parameter was the lignocellulose processing method. Even though alkaline lignin isolation provides more recalcitrant lignins, their lower aliphaticity and methoxy group content partially limit char and gas formation. Finally, enhanced monomer yields could be obtained irrespective of the ether linkage content, and a high amount of β-O-4 linkages actually showed a slightly negative effect on monomer yields. Overall, the results demonstrate that this route is particularly suitable for processing residual lignin streams.

1. Introduction

In the current world energetic scenario, where important challenges are being faced regarding an increasing energetic world demand and depletion of fossil resources, the potential of lignocellulosic biomass as an alternative and sustainable resource for energy, fuels and chemicals acquires an outstanding relevance for future biorefinery schemes (Özdenkçi et al., 2017; Wettstein et al., 2012). In contrast with the other two main biopolymers in lignocellulose (cellulose and hemicellulose), lignin conversion towards added-value products is lagging behind (Rinaldi et al., 2016). Even though it is the most abundant source for renewable aromatics, lignin is still mostly utilized solely for heat and power production through combustion (Calvo-Flores and Dobado, 2010). This underutilization is related to the complexity of the

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lignin structure, consisting of three main aromatic units, which differ on their methoxylation degree: p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, connected through a variety of (mostly ether-type) linkages that can occur depending on the biomass source and processing conditions (Constant et al., 2016; Sun et al., 2018).

Technical lignins are cheap and commercially available in large quantities, which make them attractive feedstock for valorization towards chemicals (Zakzeski et al., 2010). However, their structural heterogeneity demands advanced insight into their reactivity in order to optimize high-value applications (Pang et al., 2017; Park et al., 2018), but detailed structural analysis in combination with reactivity studies are generally lacking in literature, even though this information is crucial for developing more efficient lignin applications (Deuss et al., 2017; Naseem et al., 2016). Due to their higher quality and purity, organosolv (sulfur-free) lignins are in principle preferred for biorefinery processing, and have attracted the largest share of research attention over the past years (Hashmi et al., 2017; Kuznetsov et al., 2017). However, most of the available commercial lignin is derived from Kraft pulping, mainly generated in the paper industry (Azadi et al., 2013). To date, several works have reported the performance of different types of lignins (either different biomass sources or originated from different isolation processes), but the dependence of their reactivity on their structure and composition is still not quite understood.

From all the lignin conversion techniques available for the production of chemicals, reductive methods like hydrotreatment stand out due to their capacity to produce relatively stable products with a lower oxygen content, simultaneously performing the last two stages of the traditional fractionation-depolymerization-upgrading sequence for lignin valorization (Schutyser et al., 2018). Traditionally, lignin hydrotreatment has been carried out in the presence of a solvent, mostly to avoid recondensation of intermediate radicals (Agarwal et al., 2017; Narani et al., 2015). However, it is known that solvents are not bystanders in the catalytic conversion of lignin, and solvent recycling can be challenging and costly (Wang and Rinaldi, 2012). One method that circumvents this issue is the development of solvent-free strategies. Nevertheless, examples of solvent-free hydrotreatment studies are still scarce in literature. Meier et al. (1992) performed a solvent-free hydropyrolysis of different lignins and reported lignin oil yields of 61.6 wt % using a NiMo/SiO_2-Al_2O_3 catalyst with a monomer yield of 21.8 wt% when processing organocell lignin. Our group recently reported a solvent-free hydrotreatment approach using supported Ru, Pd and Cu catalysts for Alcell® lignin obtaining lignin oil yields of 78 wt%, with a monomer yield of 22.1 wt% using a Ru/TiO_2 catalyst (Kloekhorst and Heeres, 2015). Furthermore, sulfided NiMo and CoMo catalysts were studied by Kumar et al. (2015) for the solvent-free hydrotreatment of Kraft lignin achieving a lignin conversion of 65–87% and a monomer yield of 55 wt% using a NiMo/AC catalyst.

The conversion of low-value feedstock requires cheap and sturdy catalysts from an economic perspective. In this context, Fe-based catalysts like limonite iron ore, which have traditionally been applied for direct coal liquefaction (Kaneko et al., 2002), have also recently shown promising features for the catalytic conversion of bio-derived feedstock in reforming (Zhao et al., 2017) and cracking (He et al., 2018) processes. Specifically for lignin conversion through hydrotreatment, Agarwal et al. (2017) recently explored the possibilities of a limonite catalyst for solvent-free lignin hydrotreatment obtaining a lignin oil yield of 33.7 wt% with a total 30.9 wt% monomer yield at 450 °C. Furthermore, in a work by Breunig et al. (2017), Fe-based catalysts also proved to be beneficial in order to prevent the formation of char in favor of higher oil yields, in comparison with Mo-based catalysts in the hydrogenolysis of different technical lignins in a solvent-free environment. This type of catalysts also present the advantage of being activated in their sulfided form, which makes them more robust when dealing with sulfur containing feedstock, like lignins derived from popular sulfur-based isolation methods (like lignosulfonate and Kraft techniques).

Table 1
Designation, biomass source and isolation procedure for all the lignins used in this study.

Code	Biomass source[a]	Extraction
Kraft AT	SW	Kraft (alkaline)
Kraft M	SW	Kraft (alkaline)
Soda	G/S (wheat straw and Sarkanda grass)	Soda (alkaline)
Alcell	Mixed HW (maple, birch and poplar)	Organosolv (ethanol–water)
Org BW	HW (beech)	Organosolv (60% ethanol- 40% water, 190 °C, 20 mM H_2SO_4)
Org WS	G/S (wheat)	Organosolv (60% ethanol- 40% water, 190 °C, 20 mM H_2SO_4)
Org P	SW (pine)	Organosolv (60% ethanol- 40% water, 190 °C, 11 mM H_2SO_4)
Org PLC	SW (pine)	Organosolv (60% ethanol- 40% water, 140 °C, 40 mM H_2SO_4)
PL	SW (pine)	Pyrolysis (water-insoluble fraction)

[a] Softwood, SW; hardwood, HW; grass/straw, G/S.

This work explores the potential of several technical lignins as a source for renewable platform chemicals through hydrotreatment in solvent-free conditions, using a cheap and readily available Fe-based limonite catalyst. Extensive lignin characterization studies (EA, GPC, FTIR, TGA, HSQC NMR, ^{13}C NMR) have allowed for gathering important information on the lignin composition and structure, which has been applied to lay relationships between the lignin structure and product distributions. This aided identification of specific desirable lignin features that link to optimal amounts of obtained high quality lignin oils, with a high content of desired monomers, specifically alkylphenolic and aromatic components.

2. Materials and methods

2.1. Lignins and catalyst

A total of nine lignins were studied, three of which were obtained from alkaline extraction processes (see Table 1 for details): two commercial softwood Kraft lignins (Kraft AT and Kraft M), and a commercial mixed grass/straw Soda Protobind 1000 lignin (Abacherli and Deppenberg, 1998) (see Constant et al., 2016, Deuss et al., 2017; Hu et al., 2016 for more information). Beech wood (Org BW), wheat straw (Org WS), and two pine lignins (Org P and Org PLC) were obtained from an acid-catalyzed ethanol-based organosolv procedure and provided by the Energy research Center of the Netherlands (ECN). Org WS and Org BW were isolated using a 60/40 wt% ethanol/water mixture at 190 °C and a catalyst concentration of 20 mM H_2SO_4, while Org P and Org PLC have been were extracted using the same ethanol/water mixture at 190 °C with a catalyst concentration of 11 mM H_2SO_4 (Org P) and 140 °C and 40 mM H_2SO_4 as a catalyst (Org PLC), respectively (Constant et al., 2016; de Wild et al., 2012; Wildschut et al., 2013). Organosolv Alcell lignin (from mixed maple, birch and poplar hardwoods) was produced by Repap (Canada) and provided by Wageningen University and Research Center (WUR, The Netherlands) (Constant et al., 2016). Pyrolytic lignin (PL) was supplied by Biomass Technology Group (BTG, Enschede, The Netherlands) and was obtained from the water fractionation of pine wood-derived pyrolysis liquids. The limonite ore catalyst was used as obtained from the nickel mine of PT Inco in Soroako (Sulawesi Island, Indonesia).

2.2. Catalytic hydrotreatment of the lignins

The catalytic hydrotreatment runs were carried out in a stainless steel 100 ml Parr Instruments Co. batch reactor equipped with a Rushton type turbine mechanical stirrer, and surrounded by a metal block containing an electrical resistance for heating purposes and

channels allowing the flow of cooling water. During the experiments, the temperature and pressure signals (provided by the control units) were monitored online and logged on a PC. For every run, the reactor was loaded with 15 g of lignin, 0.75 g of limonite, and 0.38 g of dimethyldisulfide (DMDS) for catalyst activation (1:2 DMDS to catalyst ratio). After loading the reactor, it was flushed several times with H_2 to expel air, and then pressurized to 170 bar for leak testing at room temperature. After leak testing, initial H_2 pressure was set at 100 bar and stirring was started at 1200 rpm. After that, the reactor was heated up to 450 °C at an approximate rate of 10 °C min^{-1}, and time zero was set once the reaction temperature was reached (typically after 50 min). After that, the reaction time was 4 h. These reaction conditions were established in order to give a good balance between hydrodeoxygenation level of the product oil over reduction of the aromatic rings (Agarwal et al., 2017). Once reaction time was complete, the reactor was cooled down to room temperature and the pressure at room temperature was recorded for determining the total amount of H_2 consumed during the reaction. The hydrotreatment product workup applied to retrieve the different product fractions was a solvent-based procedure in which four main product fractions were obtained: organic products, water, gas products, and char. The organic products comprise the lignin oil together with dichloromethane (DCM) and acetone solubles extracted from the catalyst and solid products. For a more detailed and schematized description of the process, the reader is referred to a previous work (Agarwal et al., 2017). Product yields and mass balances are calculated on a lignin intake basis, as specified in Eqs. (1) and (2):

$$\text{Product yield (wt\%)} = \frac{\text{Product weight}}{\text{Lignin feed weight}} 100 \quad (1)$$

$$\text{Mass balace (wt\%)} = \frac{\sum (\text{Product weight})}{\text{Lignin feed weight}} 100 \quad (2)$$

2.3. Characterization of the lignins

Elemental analyses (EA) were performed for determining the C, H, N, and S content in the lignins feeds and liquid organic sample using a Euro Vector 3400 CHN-S analyser. The amount of oxygen was calculated by the difference of CHNS.

Thermogravimetric analyses (TGA) of the different lignins were carried out in a Thermogravimetric Analyzed TGA 4000 apparatus from Perkin-Elmer. Approximately 10 mg of sample were weighed for each analysis. Temperature was raised from 30 to 900 °C at a 10 °C min^{-1} rate under an inert N_2 atmosphere (50 ml min^{-1}).

The molecular weight distributions were determined using gel permeation chromatography (GPC) analyses using a HP1100 unit equipped with three 300 × 7.5 mm PLgel 3 µm MIXED-E columns in series in combination with a GBC LC 1240 RI detector. THF was used as eluent (1 ml min^{-1}), toluene was added as a flow marker, and polystyrene standards with different molecular weight were used for calibration of the molecular weight.

^{13}C NMR and heteroatom single quantum coherence (HSQC) 2D ^{1}H-^{13}C NMR analyses were conducted in a Bruker 600 MHz spectrometer. HSQC spectra were acquired using a standard pulse sequence HSQC programme with a spectral width of (−1)-11 ppm and (−1 0)-160 ppm in the ^{1}H and ^{13}C dimensions, 4 scans and 512 increments. ^{13}C NMR spectra were acquired using an inverse-gated decoupling sequence, with a relaxation delay of 5 s, a spectral width of (−1 0)-220 ppm, and 1024 scans. Samples for HSQC NMR were prepared diluting 0.2 g of lignin in 0.8 g of dimethyl sulfoxide-d_6 (DMSO, 99.5 atom%, Sigma-Aldrich). For ^{13}C NMR samples were prepared identically and 0.1 g of chloroform was added as an internal standard (IS). The obtained data were processed using MestRenova software.

3. Results and discussion

3.1. Catalytic hydrotreatment of the lignins

A total of nine lignins were used in this study (Table 1), in order to gain a broad perspective of the performance of a variety of lignins from different biomass sources (grass/straw, softwood and hardwood) and derived from different isolation techniques (Kraft, Soda and organosolv). Among the technical lignins, two commercial Kraft lignins from softwood (Kraft AT, Kraft M), Soda lignin (from grass/straw) and 5 different organosolv (ethanol-based extraction) lignins were used: lignin from the now closed Alcell process (from mixed hardwood), two pine lignins (Org P and Org PLC, the latter extracted at less severe conditions), beech wood (Org BW) and wheat straw (Org WS) lignin (Wildschut et al., 2013). Pyrolytic lignin (PL), which is a source of lignin that is readily available at large scale from pyrolysis of biomass and subsequent aqueous fractionation, was also included (Zetterholm et al., 2018). A commercial lignosulfonate lignin (another lignin that is produced in large amounts by the paper and pulp industry) was also originally considered for this study. However, under the employed conditions this type of recalcitrant lignin did not melt due to its ionic nature (Miles-Barrett et al., 2017), and was therefore discarded as unsuitable for the production of lignin oil by the applied solventless method, which requires lignin to melt under reaction conditions.

As previously mentioned, the target product is set in alkylphenolic and aromatic compounds, due to the strategic role that these intermediate platform chemicals present in the petrochemical industry (Zakzeski et al., 2010). Besides the most commonly reported solvent-based and supercritical fluid-based processes (Kim, 2015), more innovative strategies are being developed for achieving a sustainable and efficient separation of these monomers from pyrolysis oils aiming for their final higher value applications. An example is the work by Cao et al. (2017) in which the crucial role of hydrotreatment is highlighted, by proposing a selective C−O bond hydrotreatment stage and a subsequent silica-based separation stage for phenolic compounds.

Four main product fractions were obtained from the lignin hydrotreatment experiments using limonite (450 °C, 100 bar H_2, 4 h): organic products (including lignin oil + DCM and acetone solubles), gaseous products, an aqueous phase, and char. Fig. 1 displays the product fraction distributions (expressed as wt% on lignin intake basis) and mass balances obtained from the hydrotreatment of the different lignins. Organic product yields of 22–41 wt%, aqueous phase yields of 17–23 wt%, gas yields of 16–22 wt% and char yields of 14–28 wt% were obtained. All mass balances were satisfactory (> 89%). Most of the

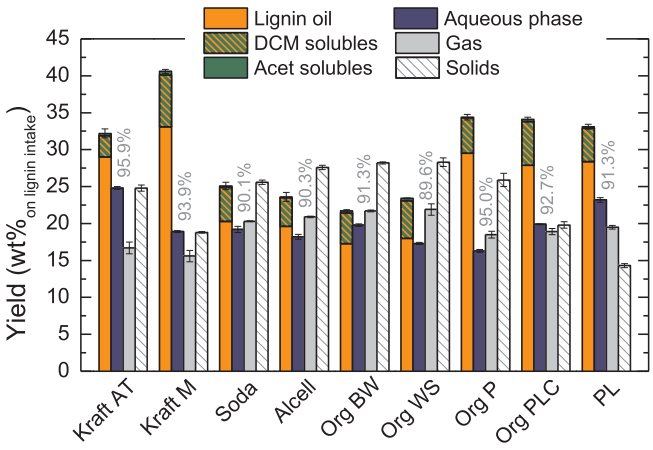

Fig. 1. Product yields and mass balances (% values) obtained on the catalytic hydrotreatment of different lignin feeds (450 °C, 4 h, 100 bar H_2 initial pressure). Error bars show standard deviation obtained from 2 to 3 separate experiments.

lignin oil (81–90% of the liquid organic products) was recovered directly from the reactor, while DCM extraction led to an additional 10–20% oil recovery, and almost a negligible amount of oil was extracted with acetone (0–0.5 wt%). The recovered gaseous products presented a significant formation of CH_4 (24–44 mol%) and CO_2 (10–15 mol%). As reported by Kloekhorst and Heeres (2015), the formation of CH_4 is a consequence of the hydrogenolysis of methoxy groups and gas phase reactions of CO and CO_2 with H_2. For evaluating the extent of the effect of incorporating a catalyst to the process, a blank reaction in no catalyst conditions with Kraft AT (as the most commercially representative of all the lignins) was performed, obtaining majoritarily char (38 wt%) with a 10.1 wt% of organic products (6.7 wt% DCM soluble + 3.4 wt% acetone soluble, no lignin oil). These results highlighted the importance of the use of a catalyst in the process for directing the products towards lighter liquid fractions. The results obtained with the limonite catalyst are in line with previous works using different sulfided catalysts in a solvent-free approach (Agarwal et al., 2017; Kumar et al., 2015) and using tetralin as solvent (Breunig et al., 2017). In the latter work, char formation was reported to be strongly affected by the ash content. However, our results show char formation was higher for some organosolv lignins, known for their high purity and very low ash content (Constant et al., 2016). This meant that other factors are likely to play a larger role in the formation of char, like for instance reaction conditions (and specifically temperature, as reported by Agarwal et al., 2017), or particularly the physico-chemical properties of the lignin themselves, which are known to be highly dependent on both the biomass source and the applied isolation method and conditions (Constant et al.,2016).

Clear performance differences have been observed based on the processed type of lignin and, while in the case of the Kraft lignins (Kraft AT, Kraft M), organosolv pine lignins (Org P and Org PLC) and pyrolytic lignin (PL) the main product fraction was the organic liquid phase (32–41 wt%), for the rest of the lignins the formation of char has been dominant (26–28 wt% solids vs 22–25 wt% organic products). Enhanced lignin oil yields and lower char formation from Kraft lignin in comparison to organosolv lignins were reported in a catalytic hydropyrolysis process using sulfided catalysts (Meier et al., 1992).

Originally, they explained their results based on a positive effect of sulfur in lignin towards enhancing catalytic activity. However, in our results such correlation to the sulfur content (obtained from elemental analysis) is not observed. For example, Soda lignin, despite its sulfur content (0.9%), still performs poorly in comparison with some sulfur-free organosolv lignins (Org P and Org PLC). Similar observations can be extracted from other works (Gillet et al., 2017), highlighting that other major lignin properties (i.e. structure properties, functional groups, *vide infra*) are playing a key role in their hydrotreatment performance. Overall, the good results obtained in terms of lignin oil yields also evidence the sturdiness of the limonite catalyst for efficiently converting a variety of lignins into platform chemicals, which is explained by the hydrogen dissociation activity of the in-situ formed pyrrhotite phase (Fe1-xS) (Agarwal et al., 2017), and aided by the presence of small amounts of Ni an Co.

The chemical composition of the produced lignin oils was analyzed by means of 2D GCxGC-FID, which allowed for clustering component regions of similar chemical nature (Kloekhorst et al., 2015). The obtained results together with the total monomer yield values are plotted in Fig. 2. Total monomer yields were of 16–29 wt% on lignin basis and, following similar trends to those observed in the product fraction distributions in Fig. 1, Kraft, organosolv pine lignins and PL led to higher monomer yields (23–29 wt%). In all cases, alkylphenolics were the main product category, with yields of 9–18 wt% on a lignin basis, and accounting for a 46–61% of the total monomers, followed by aromatic components (4–8 wt% on lignin basis), alkanes (~2 wt% on lignin basis) and oxygenated compounds (2–2.5 wt% on lignin basis). The proportion of GC detectables in the lignin oils was of 67–81%, which proves that the majority of the lignin oil is composed by volatile low

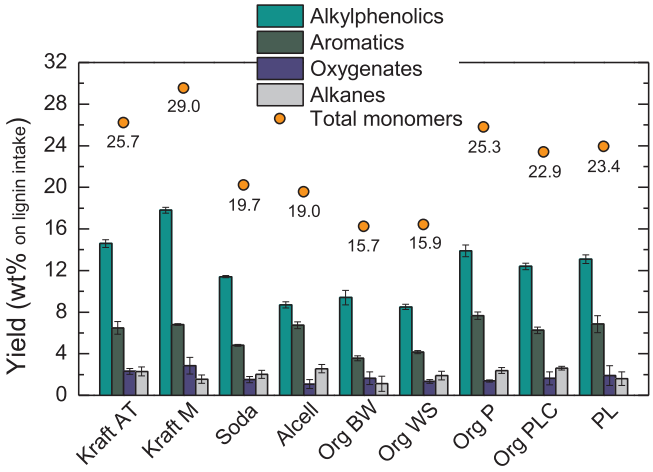

Fig. 2. Total monomer yields and composition of the lignin oils in terms of alkylphenolics, aromatics (monoaromatics and naphthalenes), oxygenates (guaiacols, catecholics and ketones) and alkanes (linear and cyclic) determined by 2D GCxGC. Error bars show standard deviation obtained from 2 to 3 separate experiments.

molecular weight components, even though there is still a heavier non-volatile fraction which could not be quantified through GC techniques. Overall, the total monomer yields achieved in this study are above the average reported in the literature in harsh hydrotreatment conditions (Schutyser et al., 2018). The produced phenolic and aromatic monomers can be used for the production of biofuels and biobased chemicals. For the former application, further hydrotreatment is a plausible strategy and, for the latter, separation is important. Recent work has shown that this can be achieved by super-critical fluid extraction as well as non-thermal separation (Cao et al., 2017; Kim, 2015). Alkylphenolics, which are the main product constituent, can serve as feedstock, like for Bisphenol A derivatives (Koelewijn et al., 2017), or can be further defunctionalized to phenol and olefins used as drop-in chemical (Verboekend et al., 2015).

GC–MS-FID analysis was used for identification of the main individual components in the lignin oils. Specifically, the main aromatic components were toluene and ethylbenzene; while in the case of the alkylphenolic compounds phenol, 2-methylphenol, 3-methylphenol, 2-ethyl-3-methylphenol were mainly detected. Almost identical chromatogram profiles were obtained for all the lignin oils. This indicates that, even though the processed type of lignin has a great impact on the lignin oil yield (as seen in Figs. 1 and 2), in all cases high-quality oils of a very similar nature are produced (with high volatility and elevated contents of alkylphenolics and aromatics), and their properties will be mostly determined by operating conditions. Our results thus show that indeed the chemical and structural nature of the feedstock can greatly condition the distribution of products, but not significantly influence the chemical nature of the produced lignin oils.

This conclusion is reinforced by the almost identical molecular weight distributions of the lignin oils shown in Fig. 3a, which also indicate the great extent of the depolymerization that can be achieved through the hydrotreatment approach. While the lignins present much wider molecular weight distributions in the 650–2200 g mol^{-1} range, the average molecular weight of the lignin oils has been decreased down to 210–230 g mol^{-1}. The wide tailing of the GPC curves (beyond 300 g mol^{-1}), confirms the presence of some heavier non-volatile oligomeric components in the lignin oil, which could not be detected by GCxGC-FID, as previously discussed from the results in Fig. 2. Components up to 220 g mol^{-1} are estimated to be identifiable by GC techniques.

In addition to the GPC analyses, elemental analysis of the different fractions reveals a similar trend. The variations in the O/C and H/C

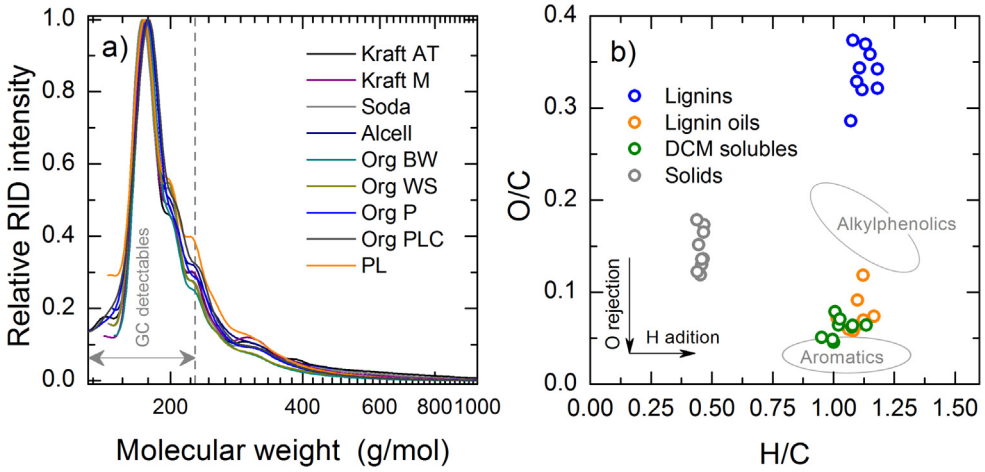

Fig. 3. a) Molecular weight distributions of the lignin oils obtained from the different lignins as determined by GPC (THF, against polystyrene standards) and b) Van Krevelen plot for the parent lignins and hydrotreatment products.

molar ratios from the parent lignins to the reaction products (as calculated from the elemental analysis data) are displayed in the Van Krevelen graph in Fig. 3b. A great decrease in the O/C ratio from the lignin feeds (0.29–0.37) to the organic product fractions (0.05–0.12) was observed, proving that hydro(deoxy)genation reactions occur in a great extent. The oxygen content is in fact reduced from 26–31% in the parent lignins to 7–13% in the lignin oils, which implies that, on average, 71% of the oxygen in lignins has been eliminated. As a consequence, the stability of these lignin oils is much higher than that of the oils obtained from lignin pyrolysis (Ardiyanti et al., 2011). The very little variations observed in the H/C ratios indicate that deoxygenation reactions are dominant over hydrogenation, which is in line with the low concentrations of saturated components detected by 2D GCxGC-FID (Fig. 2). Regarding the formed char, it presents a much condensed structure with a higher carbon content and therefore lower H/C ratio (0.44–0.47) and an important amount of oxygen (O/C: 0.12–0.18). Notably, the amount of sulfur in the obtained lignin oil could be as low as < 0.01%. The content of sulfur measured in the formed char is of 3.1–6.3%, proving that in the process not only most of the sulfur originally present in lignin will end up retained in the char, but also the sulfur added for catalyst activation (DMDS). Both are likely trapped in heavily condensed dibenzothiophene-type structures (Hita et al., 2018).

3.2. Compositional and structural characterization of the lignins

The results in the previous section suggest that there are intrinsic lignin properties that are determining for their hydrotreatment performance. As has been observed, while the type of processed lignin will not significantly condition the quality (volatility, composition) of the oil, the different lignin features (mainly determined by the biomass source and the lignin isolation process) do seem to have an impact towards enhancing or limiting the production of lignin oil and desired monomers. Identifying and understanding the role of these properties is essential in order to maximize lignin oil yields through the use of preferred lignins. In this section we have extensively characterized the lignins (TGA, 2D ^{1}H-^{13}C HSQC NMR, FTIR, ^{13}C NMR) beyond the elemental analysis already discussed in the previous section, in order to gather insights into their thermal behavior, chemical and structural properties, and explain their reactivity in hydrotreatment reactions.

TGA analysis was used to study the thermal stability of the lignins and the obtained profiles are known to be heavily dependent on the chemical bonds present in the lignins (Pang et al., 2017). The evolution of the weight loss (%) and derivative weight loss (% min^{-1}) are shown in Fig. 4a and b. The residue left by all of the lignins (Fig. 4a) was of 31–36%, with the exception of PL (20% residue), evidencing a lower polymerization degree in comparison with technical lignins, in line with a lower molecular weight. As observed from the DTG curves in Fig. 4b, lignin decomposition will take place in mostly two regions: (i) 100–160 °C, where the weight drop can be assigned to loss of moisture and highly-volatile products (Yuan et al., 2009), and (ii) 200–500 °C, where the degradation of oligomers occurs through breakage of ether-type and C—C bonds, reaching the maximum degradation rates in the 360–390 °C interval. Above 500 °C the flattened DTG signal likely indicates recondensation of aromatics (Brebu et al., 2013).

Next we turned to 2D ^{1}H-^{13}C HSQC NMR analysis of the lignins to get more insight in the chemical structure. The 2D ^{1}H-^{13}C HSQC NMR spectra for the lignins can be divided in three separate regions of interest: (i) an aliphatic side chain region (δ_C/δ_H 10–40/0.5–2.8), (ii) an oxygenated aliphatic side chain region (δ_C/δ_H 55–95/3.0–5.8), and (iii) an aromatic region (δ_C/δ_H 100–140/5.5–8.0) (Constant et al., 2016; Kumar et al., 2015). The last two are of particular interest for lignin characterization purposes, since they allow for the quantification of lignin linkages and relative contents of aromatic S-G-H units, respectively.

The quantified relative amounts of the S-G-H aromatic units for all the lignins are listed in Table 2. It was observed that both Kraft lignins, organosolv pine lignins (Org P and Org PLC) and PL consist mostly of G units (> 98%), with a very low content of H and a total absence of S units, while the rest of the lignins present a considerable amount of S units. The amounts of S-G-H units in lignin is heavily dependent on the original biomass source (Zakzeski et al., 2010) and, as expected, most of the softwood-derived lignins (Kraft AT, Kraft M, Org P, Org PLC and PL) presented a majority of G units, while hardwood lignins (Alcell and Org BW) were a mixture of S and G structures (Laskar et al., 2013), similarly to herbaceous lignins (Soda and Org WS) which are typically slightly richer in H units (Constant et al., 2016; Del Río et al., 2012). S units have been reported to present a lower thermal stability in comparison to G units, which was observed on the TGA analysis in Fig. 4, where the maximum degradation rates have been reached at slightly lower combustion temperatures for lignins consisting on both S and G units (Brebu et al., 2013).

The amount of the typical linkages in the lignins was also quantified by 2D ^{1}H-^{13}C HSQC NMR (per 100 C9 units) from the signals obtained in the oxygenated aliphatic chain region and the values are also listed in Table 2. The overall low amount of linkages measured in most of the lignins (< 12 per 100 C9 units in most cases) shows that all the lignins are already highly degraded due to the different isolation processes. The lowest linkage content was that of Soda lignin, in line with reported values (Bouxin et al., 2015; Constant et al., 2016), which also justifies its lower average molecular weight in comparison with the rest of the

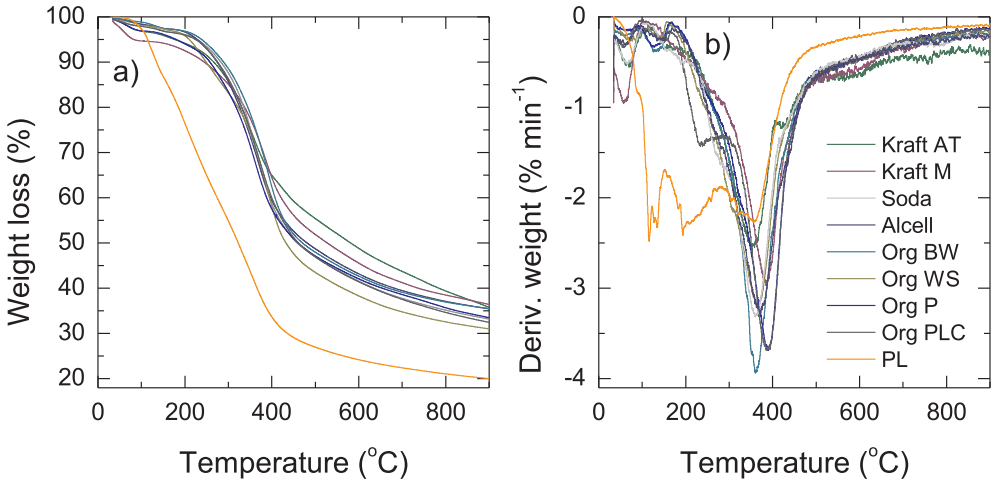

Fig. 4. a) TG and b) DTG curves obtained from the analysis of all the lignins.

Table 2
Relative amounts (%) of S-G-H aromatic units, and linkage amount (per 100 aromatic C9 units) in the lignins as determined by 2D ^{1}H-^{13}C HSQC NMR.

	S/G/H (%)	β-O-4-OH[a]	β-O-4-OR[a]	β-β[a]	β-5[a]	Total linkages
Kraft AT	0/98/2	8	0	2	1	11
Kraft M	0/99/1	4	0	4	1	9
Soda	54/41/5	2	0	1	0	3
Alcell	63/37/0	5	0	4	2	11
Org BW	67/33/0	2	2	5	3	12
Org WS	44/53/3	2	4	0	5	11
Org P	0/100/0	2	1	2	3	8
Org PLC	0/100/0	8	22	3	6	39
PL	0/100/0	–	–	–	–	–

[a] The signals from the alfa (α) positions were considered for quantification of the β-aryl-ether (β-O-4-OH stands for "normal" and β-O-4-OR for etherified, ethoxy linkages), phenylcoumaran (β-5), and resinol (β-β) linkages.

lignins (Azadi et al., 2013). Org PLC outstands with a significantly higher content of β-O-4 linkages (β-O-4-OH/R combined), due to a lower processing temperature in the extraction process in comparison with Org P, which also lead to a higher average molecular weight in comparison (2200 vs 1600 g mol^{-1}) (Wildschut et al., 2013). The predominance of etherified β-O-4-OR (R = Et) linkages in Org PLC, formed during the acidic ethanol-based fractionation (Lancefield et al., 2017), also correlates with its lower oxygen content and higher amount of carbon measured from elemental analysis, due to the ethyl chains linked to the oxygen atom connected to the α-carbon. The degradation of these β-O-4 linkages will occur fast upon increasing temperature, as deduced from the peak at 232 °C in the DTG curves in Fig. 4b, which not present for the rest of the lignins with significantly lower amounts of linkages.

When we compare the obtained structural information of the lignins to the hydrotreatment results, the aromatic S-G-H unit content seems crucial affecting the product distributions and oil compositions previously discussed in Figs. 1 and 2. We can observe how all the lignins consisting majoritarily of G units (Kraft AT, Kraft M, Org P, Org PLC and PL) have provided the best results in terms of liquid organic product yields while, when the content of S units becomes significant, these yields decrease and the formation of char becomes predominant. Even though the results are not fully conclusive in this regard, there also seems to be a positive effect of the presence of H units, but also a potential favorable role of sulfur in the lignin structure, given the better performance observed for Soda lignin in comparison to Org BW, Org WS and Alcell lignins.

The severe employed hydrotreatment conditions were sufficient for total ether-bond cleavage and lignin degradation (see Fig. 4). It should be highlighted that high cleavage-resistant technical lignins have shown comparable or even better performance to that of PL, which can be more easily depolymerized at lower temperatures, as also deduced from the data in Fig. 4. The promising results obtained with this "unconventional" lignin acquire also a high industrial significance, considering the good perspectives that the great-scale implementation of biomass pyrolysis presents (Guedes et al., 2018).

Even though 2D ^{1}H-^{13}C HSQC NMR is the best technique currently available for gathering insights into the structural features of lignin, C—C and C—O interactions can only be detected through ^{13}C NMR, which for us provided a more accurate tool for quantification compared to 2D ^{1}H-^{13}C HSQC analysis. In a typical ^{13}C NMR spectra, the main regions of interest are: the aromatic region in the 102–155 ppm range where C—H (95.8–132 ppm), C—C (132–142 ppm) and C—O (142–166.5 ppm) can be distinguished; oxygenated aliphatics in the 60.8–95.8 ppm range with a strong peak corresponding to the presence of methoxy groups at 55.2–60.8 ppm; and saturated aliphatic chains in the 0–55 ppm range (excluding the solvent) (Ben and Ragauskas, 2011). The concentration of aromatics (Arom), aliphatic saturated chains (Aliph) and oxygenated aliphatics (O-Aliph) in mmol g_{lig}^{-1} and their relative contents in lignin (%) are listed in Table 3.

The results evidence the high recalcitrance (aromaticity) of the lignins with concentrations of 11–15 mmol g_{lig}^{-1} and relative contents of 56–75%. Alkaline lignins (Kraft AT, Kraft M, Soda) show the highest aromatic content (71–75%) with the lowest relative content of aliphatics (25–29%) due to the great extent of repolymerization reactions that occur during severe alkaline pulping (Hussin et al., 2013). The lower aliphaticity of these lignins has a positive effect during hydrotreatment by preventing lignin gasification, as was observed from the results in Fig. 1. On the other hand, the relative aromatic concentrations of organosolv lignins were lower (65–68%), with the exception of Org BW (73% aromatics), which can be attributed to its hardwood origin. Org PLC was the lignin with the highest concentration of total aliphatics (9.2 mmol g_{lig}^{-1}, relative content of 42.7%), due to the high amount of saturated aliphatic chains attached to the etherified β-O-4 linkages in this lignin (Table 2). The concentration of aromatics in this lignin was also the lowest (relative content of 57%) in comparison to the rest of the technical lignins. In contrast, the very low amount of linkages in Soda lignin (Table 2) results in the lowest oxygenated aliphatic concentration of all the lignins (12.3 mmol g_{lig}^{-1}, 10.5%). The overall higher concentration of oxygenated aliphatics in organosolv lignins can be explained by the presence of etherified β-O-4 linkages in these lignins. Significant methoxy concentrations (as predicted from the intense signal in the HSQC NMR spectra of all the lignins) in the 11–15% range were quantified for the technical lignins, in agreement with previously reported values (Sumerskii et al., 2017). The highest methoxy

Table 3
Concentrations and relative contents of aromatic, side-chain aliphatics and oxygenated aliphatics in all the lignins, together with their methoxy concentrations as determined by ^{13}C NMR.

	[Arom] mmol g_{lig}^{-1}	[Aliph] mmol g_{lig}^{-1}	[O-Aliph] mmol g_{lig}^{-1}	Arom (%)	Aliph-O (%)	Aliph (%)	[MeO] $\%_{lignin}$
Kraft AT	12.4	2.1	3.0	71.0	17.0	12.0	10.5
Kraft M	13.1	2.0	2.2	75.4	12.9	11.7	11.0
Soda	13.4	2.6	1.9	74.7	10.5	14.8	12.4
Alcell	12.6	3.5	2.3	68.4	12.7	18.9	12.7
Org BW	13.7	2.0	3.0	73.1	16.2	10.7	15.0
Org WS	13.8	4.3	3.2	64.6	15.0	20.4	11.8
Org P	15.2	4.0	3.1	68.3	13.7	18.0	12.7
Org PLC	12.3	5.4	3.8	57.3	17.5	25.2	11.4
PL	11.0	5.1	3.4	56.4	17.6	25.9	4.5

concentration was that of the Org BW lignin, which also presents the highest amount of S units (Table 2). As expected, the recalcitrance of PL was lower, presenting a remarkably high concentration of oxygenated aliphatics, attributable to the high amount of ether and ketones typically present in this type of lignin (Fortin et al., 2015), also observing a significantly lower concentration of methoxy groups due to its defunctionalization in the pyrolysis process. Further defunctionalization as an effect of the hydrotreatment can be observed through ^{13}C NMR analysis of the oils, where signals corresponding to aromatic as well as aliphatic C—O bonds are almost completely absent.

3.3. Overview of observed structure–reactivity relationships

The complexity and heterogeneity of the lignins and the many factors playing a role in its hydrotreatment performance make it difficult to establish univocal and clear correlations on which parameters are key. However, the results plotted in Fig. 5 for technical lignins (PL not included) show that there is a certain tendency of the main reaction product yields with the concentration of methoxy groups and therefore, also with the amount of S-G-H units in lignin. A higher concentration of methoxy groups seems to enhance lignin gas formation in hydrotreatment reactions (Fig. 5a). In fact, the gas yields of S-G lignins were about 3–4% higher than those of G lignins, also with higher concentrations of CO and CO_2, which are directly formed from the CH_4 evolved from the hydrogenolysis of methoxy groups (Kloekhorst and Heeres, 2015). The high gas formation observed in hydrotreatment of PL (19.5 wt%, not included in the graph) despite the low methoxy concentration can be explained from its high concentration of volatile compounds which start decomposing at lower temperatures (see TGA and DTG curves in Fig. 4) and high concentration of aliphatics (measured from ^{13}C NMR, Table 2). The formation of CH_4, CO and CO_2 leads to loss of carbon in the hydrotreatment process and thus directly impact the oil yield. Char formation (as observed in Fig. 5b) is also higher for S-G lignins. Different reported reaction networks for lignin conversion (Kloekhorst and Heeres, 2015; Oregui-Bengoechea et al., 2017; Hita et al., 2018) suggest that char is formed most likely due to the repolymerization of unstable oxygenated structures derived from the S-G-H units right after the ether linkage bonds are cleaved. Consequently, S units will also be more unstable and likely to repolymerize leading to more char formation. This was also observed in TGA analysis, in which S-containing lignins reached their maximum combustion rate at slightly lower temperatures (Fig. 4). Pine-derived organosolv (Org P and Org PLC), that contain nearly exclusively G units, provide some insights on the effect of the amount of linkages in hydrotreatment. Org PLC presents a high amount of (mostly etherified) β-O-4 linkages (39 per 100 C9 units), higher molecular weight (2200 g mol^{-1} vs 1600 g mol^{-1} of Org P), and a less recalcitrant nature in comparison (as observed from ^{13}C NMR, Table 2) which, together with its lower oxygen content, led to more stable intermediate oligomers, partially preventing repolymerization reactions. However, also due to its originally lower oxygen content, and despite their very similar organic product yields (Fig. 5c), the total amount of oxygenated monomers obtained from the Org PLC lignin is limited compared to Org P (Fig. 5d), and thus the GC detectable fraction in the lignin oil was also lower for Org PLC (67.0% vs 73.5%,). Based on this, the overall slightly lower oxygen content and increased content of aliphatics of the organosolv lignins in this study (Table 3) seems to act as a limiting factor for obtaining higher yields of phenolic compounds.

Comparing G lignins and S-G lignins as a whole, Fig. 5 also shows that lignins derived from alkaline processes (particularly Kraft lignins) have performed better that organosolv lignins, producing high oil yields with limited amounts of gas and char. In this regard, the predominance of G units (Table 2) and the higher recalcitrance (aromaticity) of Kraft lignins (as determined through ^{13}C NMR, Table 2) are determining for producing a higher amount of aromatic monomers, which are also likely more stable due to the lower methoxy functionalization (10–11% of methoxy content in Kraft lignins vs 12–15% in organosolv). Previously reported characteristics such as ash (Breunig et al., 2017) and sulfur content (Meier et al., 1992) were in this study not found to significantly contribute to improved oil yields. Additionally, the molecular weight of the lignins seemed of lesser importance, as in the case of pyrolytic lignin, in which the low average molecular weight did not lead to increased oil yield compared to the kraft lignins.

4. Conclusions

A range of technical lignins provide a promising source for biorenewable platform chemicals through solventless hydrotreatment using a cheap Fe-based limonite catalyst. Oil yields of up to 41 wt% were obtained, containing mostly alkylphenolics and aromatics. Softwood alkaline G lignins are most suitable due to their higher aromaticity, lower aliphaticity and methoxy content. The amount of lignin C—O linkages does not seem to have a great impact on lignin conversion, but a significantly higher amount of etherified β-O-4 linkages can be positive for enhancing lignin oil yields, even though monomer production is limited due to the increase in aliphatic content.

Notes

The authors declare no financial interest.

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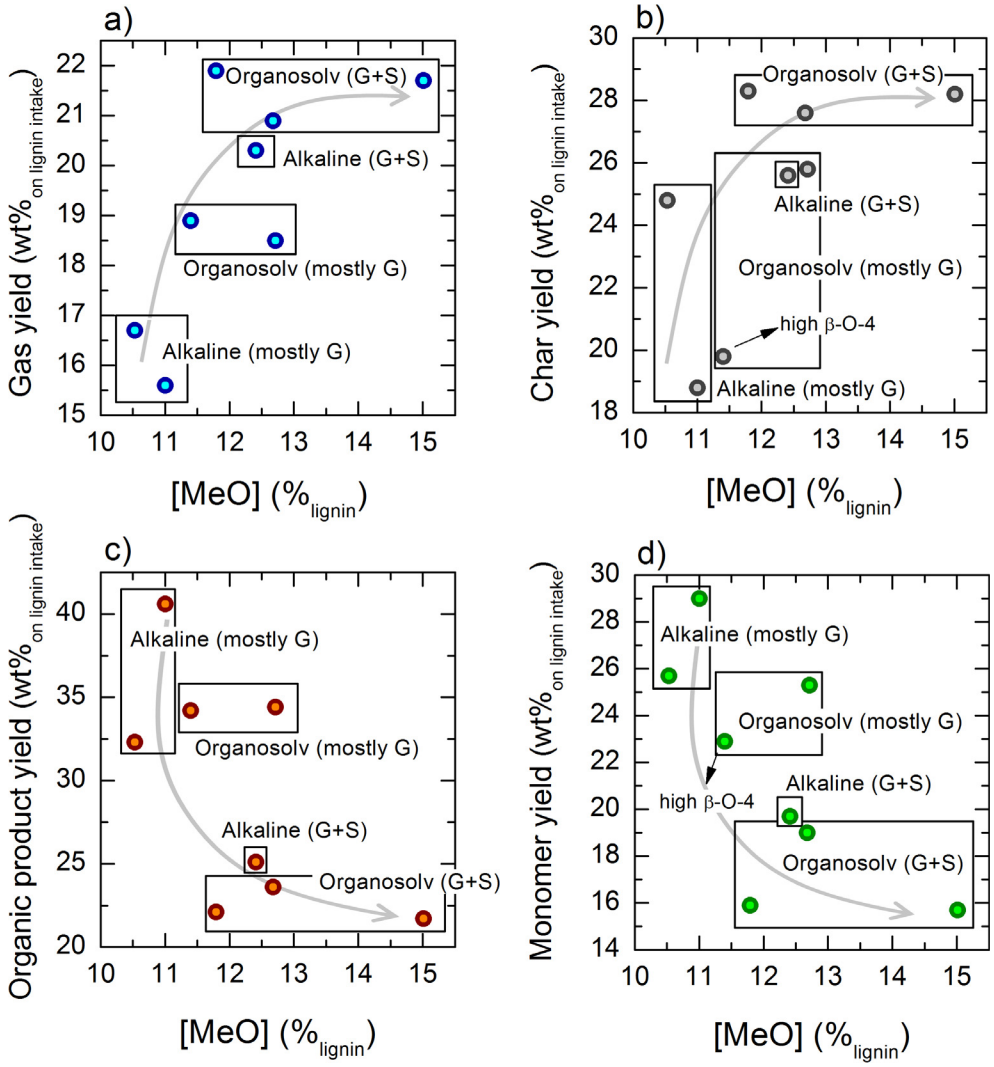

Fig. 5. Evolution of the gas, char, organic products and total monomer yields with the concentration of methoxy groups in the lignin.

framework for kindly providing most of the lignins used in this study.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.biortech.2018.07.028.

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